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Synthesis of Soluble Halogenated Polyphenylenes. Mechanism for the Coupling Halogenated  
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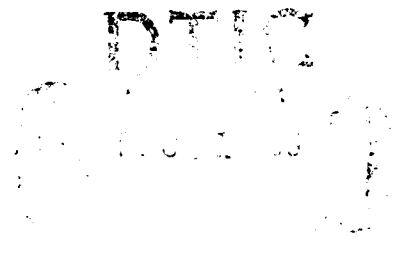
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## Synthesis of Soluble Halogenated Polyphenylenes. Mechanism for the Coupling of Halogenated Lithiobenzenes.

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### Abstract

A method for the synthesis of soluble polyphenylenes that involves the polymerization of 1-halo-4-lithiobenzenes, 1-halo-3-lithiobenzenes, and 1,3- and 1,4-dilithiobenzenes in ethereal solvents is described. The lithiobenzenes are prepared from the corresponding dihalogenated benzenes using *tert*-butyllithium. By varying the monomers and conditions used, a variety of soluble halogenated polyphenylenes can be obtained with weight average molecular weights ( $M_w$ ) as high as 6,000 with polydispersities ( $M_w/M_n$ ) equal to ~2.8. The pre-quenched polymers can exist as multilithiated polymers if 2.0 equivalents of *tert*-butyllithium are used to form the aryllithium intermediates. The polymers are usually amorphous and contain significant amounts of phenylated polyphenylene units capped with halogens. The polymers are soluble in organic solvents such as THF, chloroform, and methylene chloride. Several of the polymers exhibited low melting and glass transition temperatures. The brominated polymers are easily dehalogenated upon treatment with *tert*-butyllithium in THF at -78°C followed by quenching with water. The molecular weights of several of the brominated polymers increased upon debromination with *tert*-butyllithium. When the polymerizations were carried out in the presence of 1,3-diphenylisobenzofuran, *ortho*-benzyne intermediates were

trapped as their Diels-Alder adducts. LiH appears to be present in significant amounts upon completion of the polymerization.

## Introduction

Since the 1950s, *para*-polyphenylene (PPP) has attracted much attention as a result of its exceptional thermal, electrical, and chemical properties.<sup>2</sup> Undoped PPP is an excellent electrical insulator while the doped form can have conductivities as high as  $500 \Omega^{-1} \text{ cm}^{-1}$ .<sup>2d-f</sup> These properties have enabled PPP to be used as insulating layers in semiconductors and in the preparation of lightweight batteries.<sup>2 g</sup> However, the same structural features, namely rigidity and overall molecular symmetry, which give PPP its desirable physical and chemical properties, also hinder the polymer's ability to be processed. These polymers are insoluble in all common organic solvents and have either no, or extremely high melting or softening temperatures. Thus high temperatures and pressures are needed to fabricate the polymers into usable forms.

While most direct approaches to PPP have lead to low molecular weight insoluble material,<sup>3</sup> advances in processibility have been made through the preparation of soluble polymeric PPP precursors which, upon pyrolysis, form high molecular weight PPP.<sup>4</sup> Additional classes of substituted and branched polyphenylenes<sup>5</sup> have also been prepared which, due to a lack of polymer symmetry, are soluble in organic solvents and can exhibit low melting<sup>5h</sup> or glass transition temperatures.<sup>5f,g</sup> These materials should offer attractive alternatives to original methods for PPP preparation.

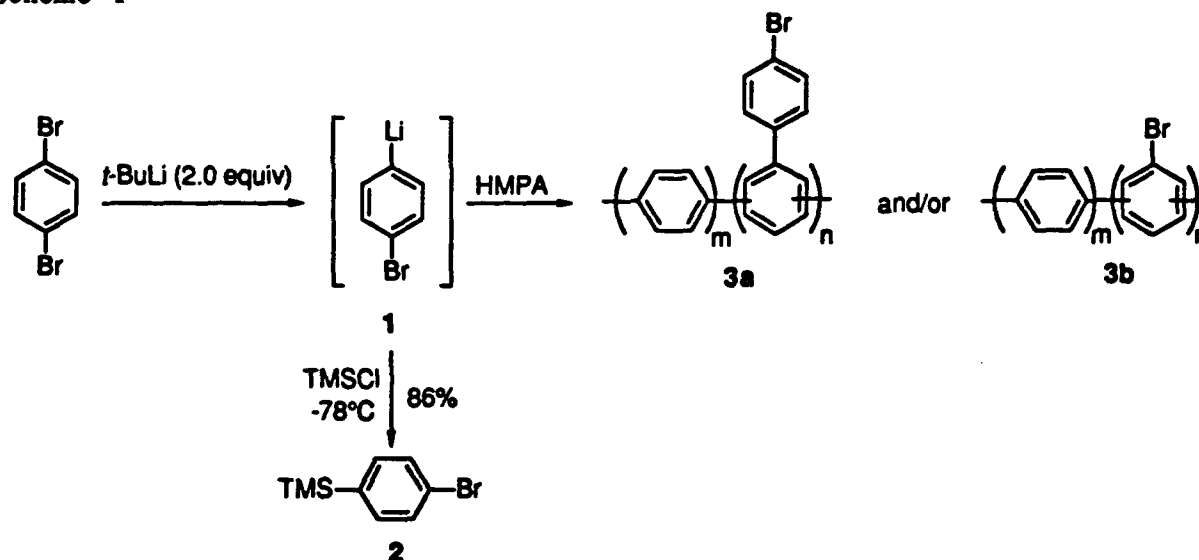
We became interested in polyphenylenes upon discovering an extremely facile Li/HMPA-promoted polymerization method in 1,4-dioxane for the synthesis of soluble brominated polyphenylenes. The polymers were predominantly *para*-linked by FTIR yet still highly soluble in organic solvents.<sup>6</sup> Recently, we reported a similar

polymerization of 1-bromo-4-lithiobenzene **1** in THF without the need for the highly toxic hexamethylphosphoramide (HMPA). This polymerization gave soluble brominated polyphenylenes containing approximately equal amounts of *para* and *meta*-linkages by FTIR analysis.<sup>7</sup> Here we report the detailed results and mechanistic implications of these polymerizations as well as the polymerizations of other mono- and dilithiated benzenes.

### Preparation of Halogenated Polyphenylenes in Dioxane with HMPA

Our initial approach to predominantly *para*-linked brominated polyphenylenes involved the formation of 1-bromo-4-lithiobenzene (**1**) in ether at -78°C by the slow addition of 2.0 equiv of *tert*-butyllithium (Scheme I). The first

Scheme I



equivalent of *tert*-butyllithium was for the lithium-halogen exchange to form **1** and *tert*-butylbromide. The second equivalent was needed for the E2 elimination of *tert*-butylbromide to afford lithium bromide, isobutylene, and isobutane. This conveniently made all the by-products unreactive, leaving no alkylhalides. While the lithium-halogen exchange reaction can be done with 1.0 equivalent of either *n*-

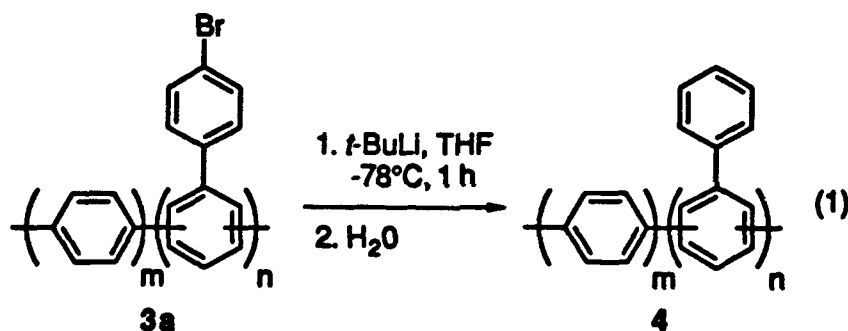
or *sec*-butyllithium, the by-products *n*-butylbromide and *sec*-butylbromide, respectively, are reactive and remain in the system. When 1.0 equiv of *n*-butyllithium was used to form intermediate 1, no polymeric products were isolated. The intermediacy of 1 in the *tert*-butyllithium reaction was confirmed in a separate experiment by the addition of chlorotrimethylsilane at  $-78^{\circ}\text{C}$  to form 1-bromo-4-(trimethylsilyl)benzene (2) in 86% isolated yield. Compound 1 was then treated at  $-78^{\circ}\text{C}$  with 1.0 equivalent of HMPA.<sup>8</sup> Upon addition of HMPA at  $-78^{\circ}\text{C}$ , the reaction solution immediately turned black and viscous. The solution was rapidly added to water in order to confirm that the polymerization was indeed occurring at these low temperatures. After precipitation from ether, a tan solid was isolated. This material had a strong FTIR absorbance at  $809\text{ cm}^{-1}$ , indicative of *para*-linked phenyl rings,<sup>9</sup> and weight average molecular weights ( $M_w$ ) of 1060 and a polydispersity ( $M_w/M_n$ ) of 2.88 relative to polystyrene standards. The solid was soluble in THF, methylene chloride, and chloroform. Intrigued by this result, we optimized the yields and molecular weights of this interesting polymerization. The results are shown in Table I.

Our optimal procedure for forming the highest weight and number average molecular weight polyphenylenes with high concentrations of *para*-linked moieties is shown in Table I, entry 1. It is similar to the procedure described above; however, the solvent used was dioxane, *tert*-butyllithium (2.0 eq) was added at  $0^{\circ}\text{C}$  and infusion of HMPA was done at  $70\text{--}80^{\circ}\text{C}$ . Upon addition of HMPA, the reaction mixture turned black and an exothermic reaction ensued. The polymerization was nearly instantaneous. Quenching with water and isolation of the ether insoluble portion gave a 25-30% yield of polymer 3 (3 appears to be predominantly 3a though a mixture of both 3a and 3b can not be ruled out) which by elemental analysis had a 25% bromide content or one bromide group for every three aryl rings. The

polymerization yields were based on the elemental data, the amount of ether insoluble material, and the amount of starting dibromide.

Size exclusion chromatography showed that 3, prepared under our optimized conditions, had  $M_w = 2400$  and  $M_w/M_n = 2.85$  relative to polystyrene standards.<sup>10</sup> It was apparent from the FTIR analysis that predominantly *para*-linked material was formed by the strong band at  $809\text{ cm}^{-1}$ . Weak bands at  $885$  and  $791\text{ cm}^{-1}$  were attributed to *meta*-linkages which destroy the crystallinity of the polymer and impart solubility. Weak branching phenyl stretches were also observed at  $762$  and  $699\text{ cm}^{-1}$ . Bands at  $1,002$  and  $1,899\text{ cm}^{-1}$  were attributed to *para*-substituted units and the presence of bromide was confirmed by the C-Br absorbance at  $1074\text{ cm}^{-1}$ .<sup>3e,9</sup> Polymer 3 showed a  $\lambda_{\text{max}}$  at  $274\text{ nm}$  in chloroform. This value was characteristic of mixtures of *para*- and *meta*-linked aryl units when compared to the reported values for oligo(phenylenes).<sup>11</sup> The  $\lambda_{\text{max}}$  in chloroform for *para*-sexiphenyl and *meta*-sexiphenyl are  $318$  and  $248\text{ nm}$ , respectively. Although powder X-ray diffraction (XRD) signals were reported for Kovacic<sup>2a</sup> and Yamamoto PPP,<sup>3e</sup> no diffraction pattern was observed for 3, consistent with the solubility of the material. Likewise, scanning electron microscopic (SEM) analysis showed the polymer to have a globular morphology pattern (Fig 1).

Since polymer 3 was soluble, debromination was easily achieved by treatment with *tert*-butyllithium in THF at  $-78^\circ\text{C}$  (eq 1). After stirring for 1 h at  $-78^\circ\text{C}$ , the



solution was quenched with water to afford the debrominated polymer 4. Elemental analysis confirmed that all the bromides had been removed. The UV spectrum of 4 showed a  $\lambda_{\text{max}}$  in chloroform of 278 nm, again consistent with mixtures of *para*- and *meta*-linked aryl rings.<sup>11</sup> No powder XRD signals were observed and SEM showed a globular morphology similar to polymer 3 (Fig 2). Surprisingly, the  $M_w$  of the polymer increased from 2400 ( $M_w/M_n = 2.85$ ) to 3180 ( $M_w/M_n = 2.80$ ) upon debromination while the material remained soluble in THF, chloroform, and methylene chloride. This observation may have resulted from the bromides in 3 causing the polymer to be retained more tightly by the SEC columns (cross-linked polystyrene). Another possibility was additional coupling of the polymer chains. The solubility of the material would suggest little or no crosslinking of the polymer chains.

Perhaps the most interesting findings of the debromination came from the FTIR analysis. The C-Br absorbance at  $1074\text{ cm}^{-1}$  was absent, further substantiating the removal of the bromide. Also the *para* band shifted from  $809\text{ cm}^{-1}$  in 3 to  $825\text{ cm}^{-1}$  in 4. This stretch was still much more intense than the *meta* band; however, the branching phenyl stretches at  $760$  and  $690\text{ cm}^{-1}$  grew in intensity. Substitution along the polyphenylene backbone as well as the incorporation of *meta*-linkages is known to increase the solubility of polyphenylenes.<sup>2b,5,11</sup> These results suggested that some of the rings in the predominantly *para*-linked backbone were possibly substituted with *p*-bromophenyl groups, as in 3a rather than 3b.

There was little if any aliphatic material present in the ether insoluble portions of 3 or 4 by  $^1\text{H}$  NMR. The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of 3 and 4 showed a broad multiplet from  $\delta$  7.0-8.0 ppm presumably due to the presence of various isomeric structural units.<sup>5g</sup> The reported CP/MAS  $^{13}\text{C}$  NMR for PPP varies according to the method of preparation. PPP prepared by the Kovacic method shows resonances at  $\delta$  139 and 128 ppm while commercial PPP has shifts at  $\delta$  143, 133, 130, 124 ppm.<sup>12</sup> The



$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) for the brominated polymer 3 showed resonances in the range of  $\delta$  124-130 and 138-142 ppm. For the debrominated polymer 4, the  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) chemical shifts were in the range of  $\delta$  124-131 and 138-144 ppm. The proton spin lattice relaxation times ( $T_1$ ) of oligo(phenylenes) are known to decrease with increased chain length, and ranges of 910 s for biphenyl to 0.48 s for PPP have been reported.<sup>13</sup> We found that the brominated polymer 3 and the debrominated polymer 4 exhibited  $T_1$  ranges of 0.4-1.6 s and 0.9-1.4 s, respectively. This also suggested that high molecular weight material was being formed during the polymerization.

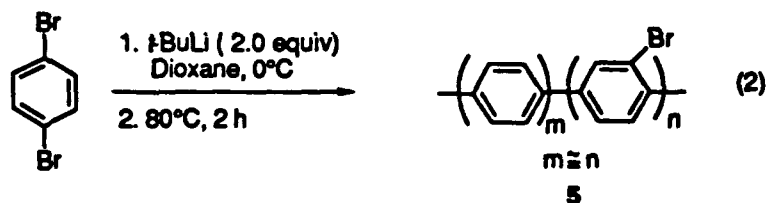
A sample of the debrominated polymer 4 doped with  $\text{FeCl}_3$  and  $\text{AsF}_5$  was subjected to 4-point probe analysis<sup>14</sup> which showed the conductivity of the doped polymer to be in the range of  $10^{-5}$  to  $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ . Good pellet formation was difficult and the conductivity was significantly less than the value for PPP prepared by the Kovacic method.<sup>2d,f</sup> The low conductivity is probably due to both the *meta*-linkages and the substituted units which are known to decrease the planarity of adjacent rings thus lowering the extended  $\pi$ -conjugation.<sup>2d</sup> Conductivity studies on solution-cast films were not possible since the material only formed brittle and irregular films presumably due to the low molecular weight and rigid aromatic backbone structure.

Thermogravimetric analysis (TGA;  $\text{N}_2$ ,  $20^\circ\text{C}/\text{min}$ ,  $50$ - $900^\circ\text{C}$ ) of polymers 3 and 4 showed similar char yields of 52% and 54% respectively. The appearance of the charred material was black and powdery, suggesting that that no significant flow had occurred during heating. Differential scanning calorimetry (DSC;  $\text{N}_2$ ,  $20^\circ\text{C}/\text{min}$ ) of polymers 3 and 4 showed no melting or glass transition points on either the first or second heating runs up to  $250^\circ\text{C}$ .

Cyclic voltammetry studies on 3 and 4 showed both polymers to be electroactive. Studies were carried out both on films and solutions of the polymer.

Polymer films were formed on the surface of a platinum electrode by dipping the electrode into THF solutions of the polymer. These studies were carried out in acetonitrile, a solvent which does not dissolve the polymer. The estimated  $E_{pa}$  value for *p*-poly(phenylene) is 1.6 V.<sup>15</sup> Irreversible anodic peak potentials ( $E_{pa}$ ) values for 3 and 4 were 1.44 and 1.45 V, respectively.<sup>16</sup> No corresponding reduction of the polymer films was observed. Solution voltammetry studies of 3 and 4 in methylene chloride showed irreversible oxidations at  $E_{pa}$  values of 2.32 and 2.24 V respectively.<sup>17</sup> The irreversibility is probably due to decomposition of the polymer as well as oxidation of the electrode at these high potentials.

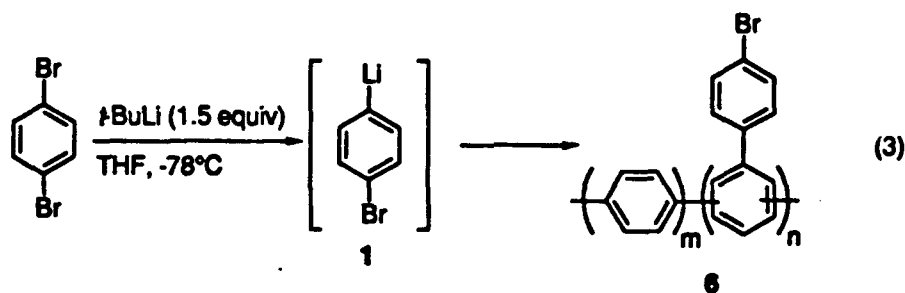
If 1 was heated to reflux at 80°C for several hours in dioxane without HMPA (eq 2), a small amount (5-7%) of a yellow solid 5 was isolated which was insoluble in



common organic solvents. 5 had no *meta*-linkages by FTIR analysis and with an intense *para* stretch at 809.7  $\text{cm}^{-1}$ . Because of the insolubility, no NMR or SEC data was obtained. Powder XRD showed 5 to be crystalline by the strong transmission bands at 4.20 Å and a weak band at 3.11 Å. Not only did the insolubility and powder XRD confirm the crystallinity of the material, but SEM analysis showed 5 to have a flake-like morphology (Fig 3). We thus concluded that 5 was probably a brominated *para*-oligophenylene. By elemental analysis, 5 contained approximately 40% bromide, or one bromide for every two rings. Attempts to relithiate 5 failed to fully debrominate the material though partial debromination could be achieved.

**Preparation of halogenated polyphenylenes in THF.**

While conducting our studies on the Li/HMPA-promoted synthesis of halogenated polyphenylenes, we found that polymers with higher concentrations of *meta*-linkages could be obtained when THF was used as the polymerization solvent (Table I, entry 5). Upon further investigation of this reaction, we found that when THF was used, these polymers could be formed without HMPA under a variety of reaction conditions (Table II). Our optimal yields and molecular weights for this system were obtained using 1.5 equivalents of *tert*-butyllithium to form **1**. A typical polymerization involved the addition of *tert*-butyllithium (24 mmol, 2.3 M in pentane) to 1,4-dibromobenzene (16 mmol) in THF (16 mL) at -78°C, thus generating 12 mmol of **1** while 4 mmol of 1,4-dibromobenzene presumably remained unreacted. The reaction was then allowed to warm to room temperature where it turned black. After stirring at room temperature for 2 h, the reaction was quenched with water. Isolation of the ether insoluble portion gave 0.61 g (50%) of polymer **6** as a tan/brown solid (eq 3). SEC showed **6** to have  $M_w = 2570$  and  $M_w/M_n = 4.06$  relative to



polystyrene while the elemental analysis showed 24% bromide or one bromide for every three aryl rings. The yields for the polymers in Table II prepared using 1.8 equivalents of *tert*-butyllithium or less were based on this elemental amount of ether insoluble material collected, and amount of *tert*-butyllithium used to form intermediate **1**.

Polymer **6** was soluble in THF, chloroform, and methylene chloride. No powder XRD signals were observed, consistent with the solubility of the material. SEM

analysis showed a globular morphology pattern. There was no aliphatic material present in the ether insoluble portion of the polymer by  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) with the aromatic signal at  $\delta$  7.2-7.9 ppm. If the polymerization yields were increased by isolation of the hexane insoluble material, aliphatic signals were observed in the  $^1\text{H}$  NMR. The  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of **6** showed peaks in the range of  $\delta$  124-135 ppm and a smaller set at  $\delta$  139-141 ppm.<sup>11</sup> The UV spectrum showed a  $\lambda_{\text{max}}$  in chloroform of 284 nm. This was again consistent with mixtures of *para*- and *meta*-linked moieties.<sup>11</sup>

The FTIR spectrum of **6** showed it to contain approximately equal amounts of *para*- (809  $\text{cm}^{-1}$ ) and *meta*-linkages (787  $\text{cm}^{-1}$ ). The previous HMPA-promoted method gave a significantly more intense *para*-linked absorbance. Additional bands at 1901 and 1002  $\text{cm}^{-1}$  were attributed to *para*-linkages. A weak *meta* band at 889  $\text{cm}^{-1}$  was also observable. The branching phenyl stretches at 762 and 698  $\text{cm}^{-1}$  were weak while the presence of bromide was confirmed by a C-Br absorbance at 1074  $\text{cm}^{-1}$ . Although no clearly distinguishable band corresponding to disubstituted *ortho*-linked units in the 750-755  $\text{cm}^{-1}$  region was observed, a shoulder on the low wave number side of the 762  $\text{cm}^{-1}$  band could be attributed to this type of substitution pattern.<sup>2b,3e,9</sup>

Interestingly, we found that when 2.0 equivalents of *tert*-butyllithium were used to convert all of the 1,4-dibromobenzene to **1**, significantly lower yields (25-30%) of ether insoluble material was collected. This could result from the formation of small amounts of 1,4-dilithiobenzene which may act as a chain terminator. Since the low molecular weight material was shown to contain aliphatics, there is the possibility that residual *tert*-butyllithium could be adding to *ortho*-benzyne intermediates (*vide infra*) which are believed to be formed during the polymerization.<sup>19</sup> We noticed that when higher amounts of *tert*-butyllithium were used, the *para* band at 809-812  $\text{cm}^{-1}$  would shift to higher wave numbers 814-817  $\text{cm}^{-1}$ .

<sup>1</sup>. The branching phenyl stretches at 760 and 690  $\text{cm}^{-1}$  also showed small increases in intensity while the C-Br absorption at 1074  $\text{cm}^{-1}$  decreased slightly suggesting that the bromide content in these polymers could be lower. This was confirmed by elemental analysis which showed one of the polymers prepared using 2.0 equivalents of *tert*-butyllithium to contain 9% bromide or one bromide for every ten phenyl rings. The yields in Table II for the polymerizations using 2.0 equivalents of *tert*-butyllithium were accordingly based on this data. Thus, not only can the conditions of the polymerization be changed to give structurally different polymers, but the amount of *tert*-butyllithium used can also change the degree of bromide content in the material.

To further probe the structure of 6, the bromides were removed by simple lithium-halogen exchange with *tert*-butyllithium at  $-78^{\circ}\text{C}$  in THF followed by a water quench to form the debrominated polymer 7. The debromination was confirmed by elemental analysis which showed the material to contain <0.5% bromide. The C-Br band in the FTIR spectrum was absent and the branching phenyl stretches increased substantially. In addition, the *para* stretch at 809  $\text{cm}^{-1}$  shifted to 824  $\text{cm}^{-1}$ . This again suggested the presence of phenylated polyphenylene previously capped with bromides at the *para* position. Interestingly, the FTIR spectrum of 7 looked remarkably similar to the IR spectrum reported by Stille for phenylated polyphenylene.<sup>2b</sup> The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) showed little or no aliphatic material with aromatic signals at  $\delta$  7.0-7.9 ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) showed signals at  $\delta$  126-131 ppm and  $\delta$  139.14 ppm. The UV spectrum showed a  $\lambda_{\text{max}}$  in chloroform at 288 nm, similar to the spectrum of 6.

When a sample of 6 having  $M_w = 1870$  with  $M_w/M_n = 2.83$  by SEC was debrominated, the value of  $M_w$  increased to 2320 with  $M_w/M_n = 2.68$ . Recall that this same pattern was observed with the debromination of 3. The increase in molecular weight could have been an effect of the bromides interacting with the crosslinked

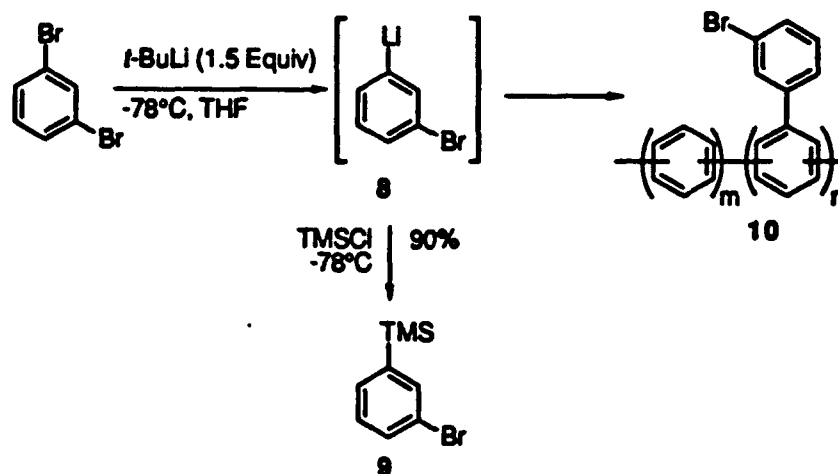
polystyrene column. However, the percentage increase in  $M_w$  was significantly greater when the debromination was carried out in the presence of HMPA ( $M_w = 1970$  with  $M_w/M_n = 3.11$  increased to  $M_w = 2770$  with  $M_w/M_n = 3.41$ ). This certainly implies that the molecular weight is increasing on debromination and even further on debromination in the presence of HMPA. It is not just an effect of the bromides causing elution rate retardation during SEC.

While the TGA ( $N_2$ ,  $20^\circ C/min$ ) of the brominated polymer 6 showed a 10% weight loss at  $385^\circ C$  and a total weight loss of 48% at  $900^\circ C$ , debrominated polymer 7 showed a 10% weight loss at  $429^\circ C$  and a total weight loss of 52% at  $900^\circ C$ . The charred materials were porous and glossy black and appeared to flow during heating.

The DSC ( $N_2$ ,  $20^\circ C/min$ ) for 6 showed broad endotherms, characteristic of melting events at  $152$  and  $175^\circ C$  on the first heating scan. The second heating scan showed possible  $T_g$ s at  $140$  and  $210^\circ C$ . The DSC thermogram for 7 showed a broad endotherm from  $170$ - $230^\circ C$  on the first heating scan and an apparent  $T_g$  at  $150^\circ C$  on the second heating scan. Since *meta*-oligophenylenes have been shown to have lower melting points than the corresponding *para*-oligophenylenes, these events are probably a result of the increased amount of *meta*-linkages and substituted units in 6 and 7 compared to the polymers derived from the Li/HMPA procedure in dioxane.<sup>11,5f-h</sup>

In order to obtain a wider variety of halogenated polyphenylenes, we investigated several additional monomer systems. The results of the polymerization of 1-lithio-3-bromobenzene (8) (Scheme II) are summarized in Table III. As before, higher yields were obtained by preparing 8 with 1.5 equivalents of *tert*-butyllithium at  $-78^\circ C$ . The intermediacy of 8 was confirmed in a separate experiment by quenching the reaction at  $-78^\circ C$  with chlorotrimethylsilane which gave a 90% yield of 1-bromo-3-(trimethylsilyl)benzene (9). By simply allowing 8 to warm to room temperature and stir 2 h, a 54% yield of polymer 10 was obtained. SEC showed

Scheme II.



polymer 10 to have higher molecular weights ( $M_w = 2850$ ) and lower polydispersities ( $M_w/M_n = 1.89$ ) than the previous polymers derived from 1,4-dibromobenzene. Higher molecular weight material could be obtained if increasing amounts of *tert*-butyllithium were used; however, the yields of ether insoluble material were again reduced.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) showed a broad aromatic signal at  $\delta$  6.9-7.9 ppm with no aliphatic material present. If, however, the yields were increased by collecting hexane insoluble fractions, aliphatics were observed in the  $^1\text{H}$  NMR. The  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) of 10 showed signals at  $\delta$  122-132 and  $\delta$  139-144 ppm. The UV data showed a  $\lambda_{\text{max}}$  in chloroform of 256 nm, consistent with predominantly *meta*-linked aryl rings.<sup>10</sup> FTIR analysis of 10 confirmed that the polymer was predominantly *meta*-linked by the intense absorbance at  $782\text{ cm}^{-1}$ . The *para*-linked band was weak and had shifted to higher wave numbers at  $839\text{ cm}^{-1}$  confirming that the amount of *para*-linkages in the polymer was low. Branching phenyl stretches at  $755$  and  $700\text{ cm}^{-1}$  were also observed. The C-Br absorption was evident at  $1074\text{ cm}^{-1}$ ; however, it was noticeably weaker than the previous polymers prepared from 1-bromo-4-lithiobenzene (1). The branching phenyl stretches were also much more intense than with earlier systems. All of these factors suggested a lower bromide

content. Elemental analysis showed 10 prepared using 1.5 equivalents of *tert*-butyllithium to contain 12% bromide or one bromide for every eight phenyl rings. This was significantly lower than the previous polymers prepared from 1,4-dibromobenzene. When increased amounts of *tert*-butyllithium were used to form intermediate 8, there was a noticeable decrease in the C-Br band at  $1074\text{ cm}^{-1}$  and an increase in the branching phenyl stretches at  $755$  and  $700\text{ cm}^{-1}$ . Elemental analysis showed that when 1.8 equivalents of *tert*-butyllithium were used, the amount of bromide in these polymers could be reduced to only 8% or one bromide for every eleven aryl rings. When 2.0 equivalents of *tert*-butyllithium were used, the bromide content decreased to 2% or one bromide for every forty one aryl rings. The bromide content for the polymers prepared from 1,3-dibromobenzene was therefore considerably less than the polymers prepared from 1,4-dibromobenzene and the effect of the increased *tert*-butyllithium on the bromide content was more pronounced.

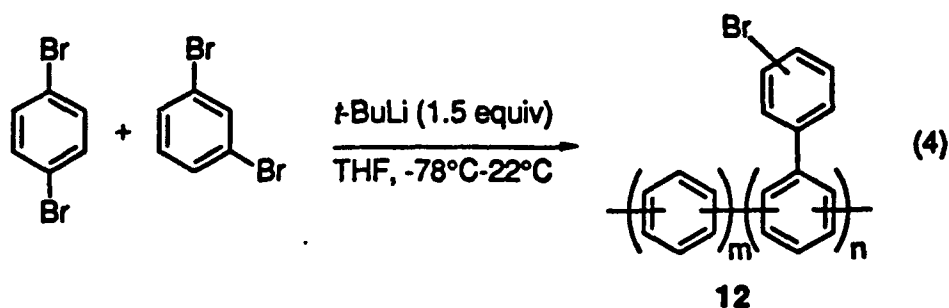
Debromination of 10 was achieved upon re-lithiation with *tert*-butyllithium in THF at  $-78^{\circ}\text{C}$  followed by quenching with water to afford 11. Again the molecular weight of the polymer increased from  $M_w = 2360$  with  $M_w/M_n = 2.23$  to  $M_w = 2890$  with  $M_w/M_n = 1.72$  suggesting further coupling of the polymer chains. Note the decrease in polydispersity for 11. Since an increase in the amount of *meta*-linkages is known to improve solubility in polyphenylenes, these predominantly *meta*-linked polymers are more soluble, thereby allowing the lower molecular weight material to be removed during the ether precipitations and, in turn, lower the polydispersities. Elemental analysis confirmed that all the bromide content in 10 had been removed on conversion to 11. The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) of 11 showed a broad multiplet from  $\delta$  6.8-8.0 ppm, similar to 10. If hexane insoluble portions were checked by  $^1\text{H}$  NMR, small amounts of aliphatic material were observed. The  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ) was also similar with broad peaks at  $\delta$  140-142 and 125-132 ppm. The UV



spectrum showed  $\lambda_{\max}$  at 252 nm, consistent with predominantly *meta*-linked material **11**

The TGA ( $N_2$ , 20°C/min) of brominated polymer **10** showed 10% weight loss at 434°C and a char yield of 59% at 900°C. The debrominated polymer **11** had a 10% weight loss at 468°C and a char yield of 55% at 900°C. The DSC ( $N_2$ , 20°C/min) analysis of **10** and **11** showed no melting or glass transition events on either the first or second heating runs up to 250°C. However, these materials did appear to flow by visual observation of the charred material.

When equal amounts of 1,4- and 1,3-dibromobenzene were treated with 1.5 equivalents of *tert*-butyllithium in THF at -78°C and allowed to warm to room temperature and stir for 2 h, a 62% yield of polymer **12** ( $M_w = 3340$ ,  $M_w/M_n = 3.0$ ) was obtained (eq 4). **12** was also predominantly *meta*-linked by FTIR analysis as

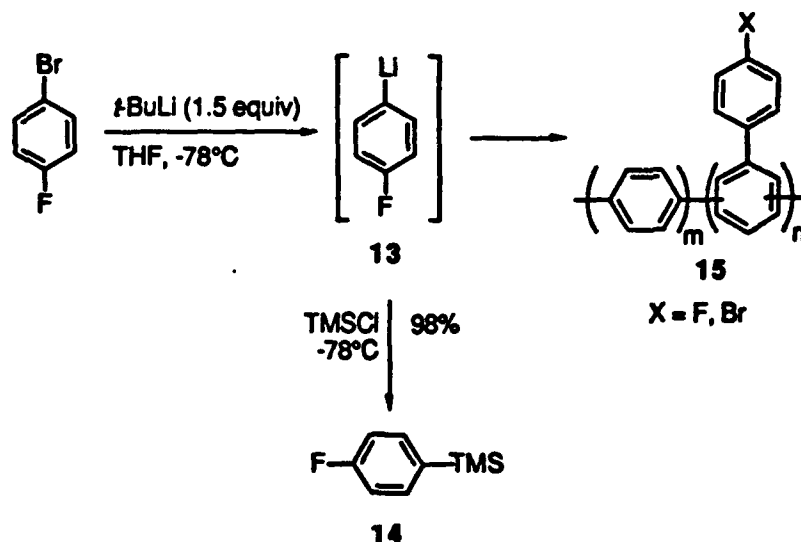


evidenced by the strong *meta* band at 785  $\text{cm}^{-1}$ . The *para* band at 825  $\text{cm}^{-1}$  was weak and had shifted to higher wave numbers compared to the previous polymer prepared using 1,4-dibromobenzene. The UV spectrum showed a  $\lambda_{\max}$  in chloroform accordingly at 262 nm, a value between that of **6** at 284 nm and **10** at 252 nm. Elemental analysis showed the material contained approximately 13% bromides or one bromide for every seven aryl rings by elemental analysis.

We attempted to make soluble fluorinated and chlorinated polyphenylenes using 1,4-difluorobenzene and 1,4-dichlorobenzene. However, when 1,4-difluorobenzene was treated with 2.0 equivalents of *tert*-butyllithium at -78°C in THF

then allowed to warm to room temperature and stir 2 h, a brown insoluble solid containing mixtures of *para* (824  $\text{cm}^{-1}$ ) and *meta* (874  $\text{cm}^{-1}$ ) linkages was obtained. When 1,4-dichlorobenzene was treated with 2.0 equivalents of *tert*-butyllithium at -78°C in THF, followed by addition of HMPA at 65°C, a brown insoluble solid was obtained. This material also contained mixtures of *para* (816.2  $\text{cm}^{-1}$ ) and *meta* (790.5  $\text{cm}^{-1}$ ) linkages. These results were not surprising since fluorides and chlorides generally do not undergo facile lithium-halogen exchange reactions.<sup>19</sup> These materials are probably highly crosslinked. Soluble fluorinated polymers could be obtained, however, when the mono-lithiated substrate of 1-bromo-4-fluorobenzene **13** was stirred at room temperature in THF (Scheme III). The intermediacy of **13** was

Scheme III.



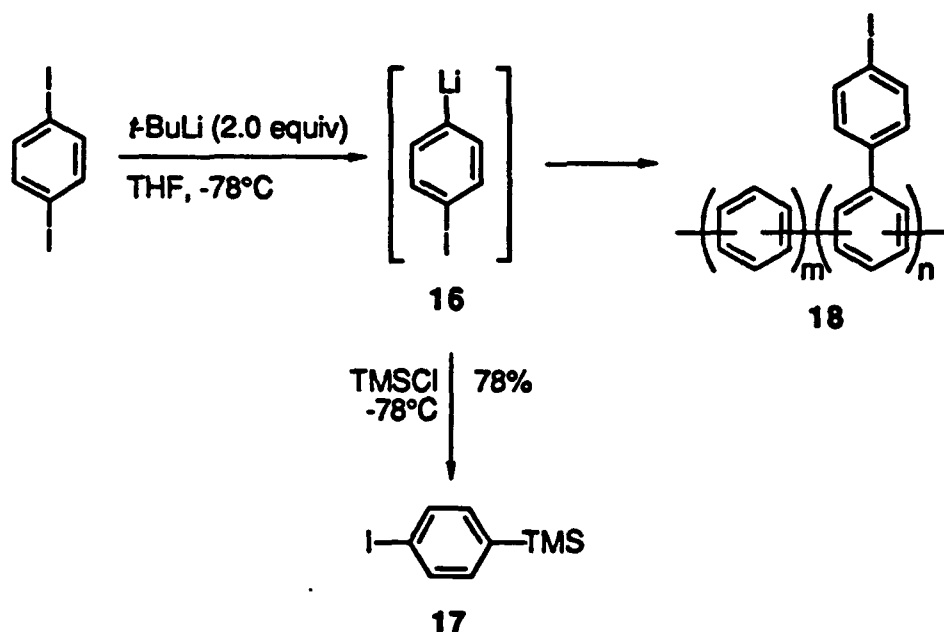
confirmed in a separate experiment by quenching the reaction solution at -78°C with chlorotrimethylsilane to give a 98% yield of 1-fluoro-4-(trimethylsilyl)benzene (**14**). The results of the polymerization are shown in Table IV. The optimal results again involved treatment of 1-bromo-4-fluorobenzene with 1.5 equivalents of *tert*-butyllithium in THF at -78°C followed by stirring at room temperature for 2 h. This

gave a 51% yield of polymer 15 which had  $M_w = 6000$  and  $M_w/M_n = 2.83$ . Elemental analysis of 15 showed it to contain both bromide (5% or one for every twenty aryl rings) and fluoride (4% or three for every twenty phenyl rings).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) showed no aliphatic material in the ether insoluble portion with aromatic signals at  $\delta$  6.8-7.9 ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) showed signals at  $\delta$  115-116, 126-129, and 139-142 ppm. FTIR analysis showed that the polymer contained mixtures of *para*-linkages at  $818\text{ cm}^{-1}$  and *meta*-linkages at  $790\text{ cm}^{-1}$ . The *para/meta* ratio did appear to favor *para*-linkages, but not as much as the earlier polymers prepared in dioxane. The C-Br absorbance at  $1074\text{ cm}^{-1}$  was weak while a stretch at  $1158\text{ cm}^{-1}$  was attributed to the C-F moieties.<sup>20</sup> If increased amounts of *tert*-butyllithium were used, the C-Br absorbance at  $1074\text{ cm}^{-1}$  did appear to weaken while the branching phenyl stretches increased in intensity. There was also a noticeable shift in the *para* band at  $818\text{ cm}^{-1}$  to higher wave numbers ( $820\text{-}821\text{ cm}^{-1}$ ). This would again suggest that the halogen content in these polymers was lowered using larger amounts of *tert*-butyllithium. TGA analysis ( $\text{N}_2$ ,  $20^\circ\text{C}/\text{min}$ ) of 15 showed a 10% weight loss at  $449^\circ\text{C}$  and char yields of 59% at  $900^\circ\text{C}$ . DSC analysis ( $\text{N}_2$ ,  $20^\circ\text{C}/\text{min}$ ) showed no melting or glass transition events up to  $230^\circ\text{C}$ . However, the charred material was glossy black and did appear to flow on heating.

Soluble iodinated polyphenylenes 18 were also prepared in THF from 1-lithio-4-iodobenzene (16) (Scheme IV). The results are shown in Table V. Unlike the previous systems, our optimal conditions for forming polymer 18 involved treatment of 1,4-diiodobenzene with 2.0 equivalents of *tert*-butyllithium at  $-78^\circ\text{C}$  in THF. The intermediacy of 16 was confirmed in a separate experiment by quenching the reaction solution with chlorotrimethylsilane at  $-78^\circ\text{C}$  to give a 78% yield of 1-iodo-4-trimethylsilylbenzene (17). If the reaction solution was allowed to warm to room temperature and stir for 2 h, yields of up to 65% of polymer 18 with  $M_w = 4250$  and  $M_w/M_n = 3.05$  were obtained. The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) showed no aliphatic

material in the other insoluble portion with aromatic signals at  $\delta$  6.8-8.0 ppm. The UV spectrum showed a  $\lambda_{\text{max}}$  in chloroform at 276 nm. The FTIR spectrum of 18 was similar to the one obtained from the polymerization of 1-bromo-4-lithiobenzene (1) in THF. When 1.5 equivalents of *tert*-butyllithium were used, the *para* and *meta*

Scheme IV.

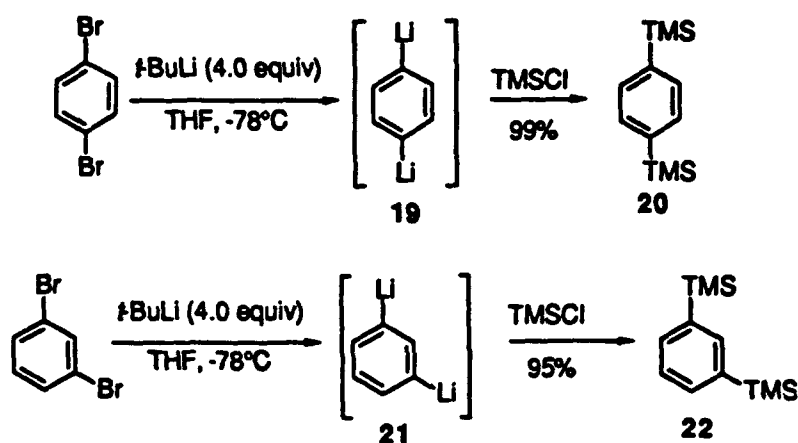


bands at 805 and 781  $\text{cm}^{-1}$ , respectively, were strong and approximately equal in intensity. Upon moving to 2.0 equivalents of *tert*-butyllithium, however, both bands became much weaker and the *para* band shifted to 825  $\text{cm}^{-1}$  while the branching phenyl bands at 758 and 697  $\text{cm}^{-1}$  increased in intensity. A noticeable decrease in intensity for the C-I absorbance<sup>3e</sup> at 1064  $\text{cm}^{-1}$  was also apparent when 2.0 equivalents of *tert*-butyllithium were used. Elemental analysis showed that 18 prepared using 2.0 equivalents of *tert*-butyllithium contained 10% iodide or approximately one iodide for every fourteen phenyl rings. When 1.5 equivalents of *tert*-butyllithium was used to form intermediate 16, the iodide content increased to 36% or one iodide for every three aryl rings. DSC analysis ( $\text{N}_2$ , 20°C/min) for 18

showed no transitions on either the first or second heating scans to 230°C. TGA analysis (N<sub>2</sub>, 20°C/min) showed a 10% weight loss at 322°C and char yields of 46% at 900°C. Visual analysis of the charred material did indicate that the material flowed during heating.

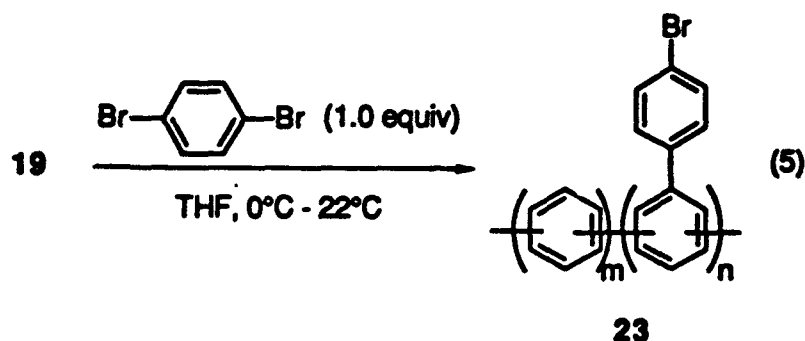
Dianions of 1,4-dibromobenzene and 1,3-dibromobenzene can also be cleanly generated in ethereal solvents like THF or ether (Scheme V) upon addition to 4.0

Scheme V.



equivalents of *tert*-butyllithium in THF at -78°C. The intermediacy of these dianions was confirmed by quenching the reactions at -78°C with TMSCl to afford excellent yields of the disilylated adducts 20 and 22.<sup>19b</sup>

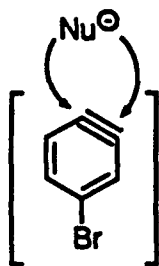
Interestingly, when 19 was prepared in THF and allowed to warm to room temperature and stir 16 h, no polymeric products were isolated after quenching the reaction solution with chlorotrimethylsilane. Instead, an 81% isolated yield of 20 was obtained. Thus, without the presence of aryl halides, the polymerization does not occur. When 19 or 21 was treated with 1,4-difluorobenzene, 2,5-dichloropyridine, or 2,6-dichloropyridine, insoluble polymeric products resulted. Soluble brominated polyphenylene 23 was produced from the copolymerization of 1,4-dilithiobenzene (19) and 1,4-dibromobenzene (eq 5).



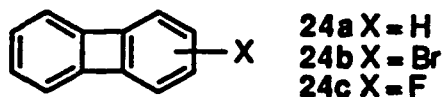
The polymerization procedure is similar to the polymerizations discussed earlier but it involves addition of the dilithio species to the dihalogenated aromatic at  $0^\circ\text{C}$  in THF. The reaction is then allowed to warm to room temperature and stir overnight. Isolation of the ether insoluble material gave a 53% yield of polymer 23 which is remarkably similar to the polymers prepared from 1-bromo-4-lithiobenzene (1). The yield was based on the amount of dihalogenated aromatics used and the elemental analysis which showed the polymer to contain approximately 11% bromide or one bromide for every nine phenyl rings. 23 had  $M_w = 3110$  with  $M_w/M_n = 3.6$  relative to polystyrene standards. FTIR analysis showed approximately equal intensity *para* and *meta* bands at  $818$  and  $789\text{ cm}^{-1}$ , respectively. The  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) showed a broad aromatic signal at  $\delta$  7.0-7.9 with little or no aliphatics. DSC analysis ( $\text{N}_2$ ,  $20^\circ\text{C}/\text{min}$ ,  $50$ - $250^\circ\text{C}$ ) showed a broad endotherm at  $165$ - $240^\circ\text{C}$  on the first heating scan. Apparent  $T_g$ s were observed at  $150^\circ\text{C}$  and  $220^\circ\text{C}$  on the second heating scan. The TGA ( $\text{N}_2$ ,  $20^\circ\text{C}/\text{min}$ ) showed 10% weight loss at  $451^\circ\text{C}$  and a char yield of 58% at  $900^\circ\text{C}$ . When 23 was debrominated with *tert*-butyllithium in THF at  $-78^\circ\text{C}$ , the *para* band shifted to  $820\text{ cm}^{-1}$  while the branching phenyl stretches grew in intensity confirming that the structure was indeed similar to the previous polymer systems. Surprisingly, the molecular weight dropped slightly to  $M_w = 2950$  with  $M_w/M_n = 3.5$ . The lower bromide content in this polymer may have hindered additional coupling of the polymer chains.

## Mechanistic Findings

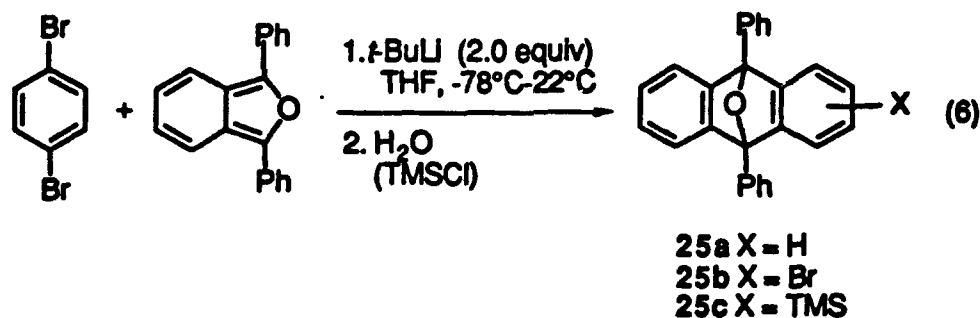
There are several features of these polymerizations which suggest that *ortho*-benzyne<sup>21</sup> intermediates are involved. The first and most obvious is the presence of both *meta*- and *para*-linkages in all of the polymers. If an *ortho*-benzyne intermediate as shown below was formed, it could be attacked by an aryllithium species at a position *meta* or *para* to the remaining bromide.



Biphenylene and substituted biphenylenes are also known to form during reactions involving *ortho*-benzyne intermediates.<sup>21a,22</sup> The mass spectrometric (MS) analysis of the ether soluble fractions from polymerizations of 1-bromo-4-lithiobenzene (1) showed  $M^+$  peaks corresponding not only to biphenylene 24a at 151 amu, but also brominated biphenylene 24b at 230 and 232 amu. The MS analysis of the ether soluble portions from the polymerization of 1-fluoro-4-lithiobenzene 13 showed fluorinated biphenylene 24c at 170 amu.



*Ortho*-benzyne intermediates can also be trapped as their Diels-Alder adducts.<sup>21a,23</sup> When 1-bromo-4-lithiobenzene (1), prepared using 2.0 equivalents of *tert*-butyllithium, was allowed to warm to room temperature for 2  $\mu$  in the presence of 1,3-diphenylisobenzofuran followed by quenching with water, we searched for the corresponding Diels-Alder adducts (eq 6). Attempts to cleanly isolate and purify



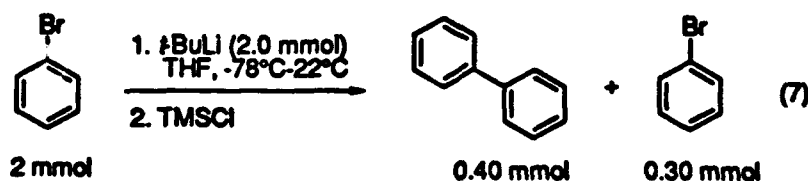
the Diels-Alder adducts by column chromatography [alumina, benzene, ether (1/1)] were unsuccessful since they appeared to decompose on both alumina and silica gel. However, when the partially decomposed yellow materials ( $R_f = 0.9$  in 1:1 benzene/ether) were subjected to MS analysis,  $M^+$  at 346, 424, and 426 amu were observed. These molecular weights did indeed correspond to the Diels-Alder adducts 25a ( $\text{C}_{26}\text{H}_{18}\text{O}$ ) and 25b ( $\text{C}_{26}\text{H}_{17}^{79}\text{BrO}$ ,  $\text{C}_{26}\text{H}_{17}^{81}\text{BrO}$ ). Small amounts of 1,2-dibenzoylbenzene were also obtained from a separate fraction ( $R_f = 0.6$  in 1:1 benzene/ether). A similar *ortho*-benzyne trapping reaction was then repeated; however, this time, the reaction was quenched with TMSCl. Although  $^1\text{H}$  NMR analysis of the crude product did indicate the presence of small amounts of silylated material, purification attempts were again unsuccessful. The peaks in the aromatic region were broadened suggesting that oligomeric and or polymeric material had been formed. The MS of the crude product did, however, show  $M^+$  at 418 amu corresponding to 25c ( $\text{C}_{29}\text{H}_{26}\text{OSi}$ ).

The presence of silylated material was indeed surprising since many of our higher molecular weight polymers prepared using 1.5 equivalents of *tert*-butyllithium were quenched with TMSCl and no silylated material was observed.<sup>7</sup> Thus it is apparent that the polymers prepared using 1.5 equivalents of *tert*-butyllithium were not polyolithiated. We then polymerized 1-bromo-4-lithiobenzene (1) using 2.0 equivalents of *tert*-butyllithium. After stirring at room temperature for 2 h, the reaction was quenched with TMSCl. This time silylated material was observed



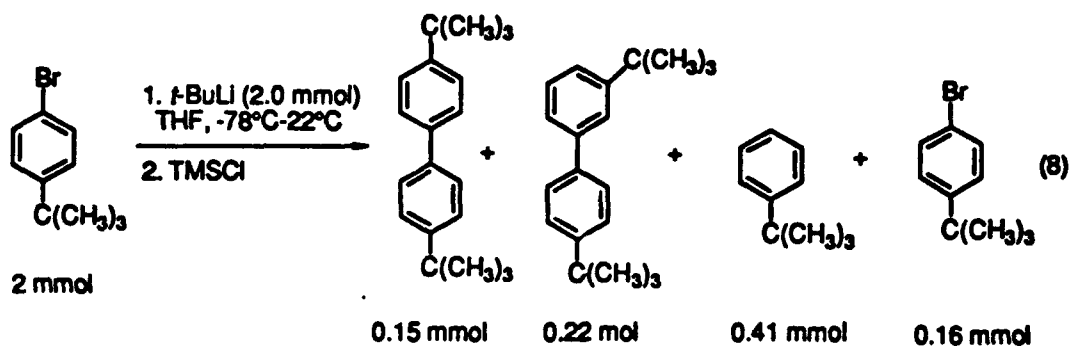
in the  $^1\text{H}$  NMR spectra of both the ether insoluble material and the ether soluble portions. Thus our polymers can exist as lithiated systems if conditions are adjusted. This may enable the polymer to be functionalized *in situ* with a variety of electrophiles. This also explains the lower bromide content in many of the polymers prepared using 2.0 equivalents of *tert*-butyllithium.

A mixture of fluorobenzene and phenyllithium in ether and THF at temperatures greater than  $-25^\circ\text{C}$  is known to produce 2-lithiobiphenyl via an *ortho*-benzyne intermediate. The process involves abstraction of the proton *ortho* to fluoride by phenyllithium followed by elimination of LiF to give *ortho*-benzyne. A second equivalent of phenyllithium then adds to the *ortho*-benzyne giving 2-lithiobiphenyl. If substituted fluorobenzenes are used, isomeric mixtures of lithiobiphenyls are produced.<sup>21a</sup> In order to probe whether similar deprotonations leading to *ortho*-benzyne intermediates may be occurring in our polymerizations, we generated phenyllithium in the presence of bromobenzene by treating *tert*-butyllithium (2 mmol) with one equivalent of bromobenzene (2 mmol) in THF at  $-78^\circ\text{C}$  to produce a 1:1 mixture of bromobenzene and phenyllithium (recall 4 mmol of *tert*-butyllithium would be necessary for the complete conversion of 2 mmol of the bromobenzene to phenyllithium). The reaction solution was then allowed to warm to room temperature and stir 16 h before quenching with TMSCl (eq 7). This gave 0.40



mmol of biphenyl (GC yield using undecane as an internal standard with the response ratio determined from an authentic sample) while 0.30 mmol of bromobenzene was recovered. No low molecular weight silylated aromatics were detected by the GC (comparing against authentic silylated aromatics) or by the GCMS.

Benzene would remain undetected being in the solvent front. Quatraphenyl species would be beyond the GC range screened. Similar studies were then conducted using 1-bromo-4-*t*-butylbenzene (2 mmol) (eq 8). 4,4'-Bis(*tert*-butyl)biphenyl (0.15 mmol) and 3,4'-bis(*tert*-butyl)biphenyl (0.22 mol) were obtained along with *tert*-

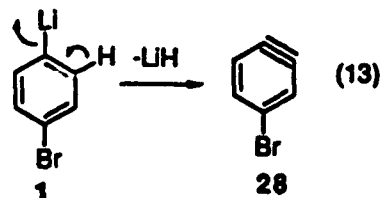
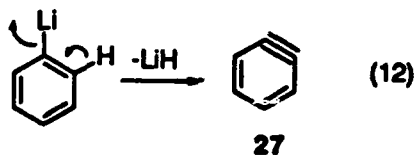
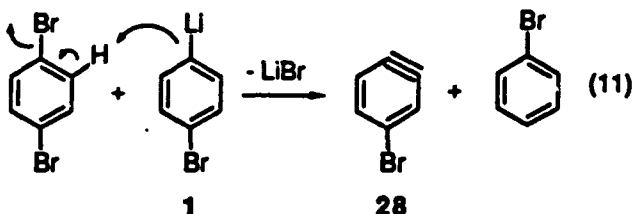
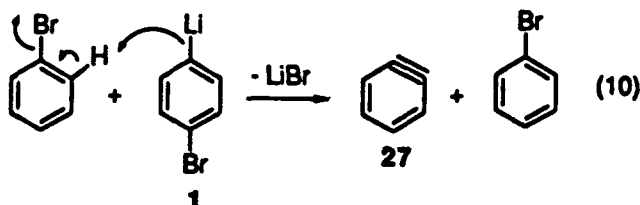
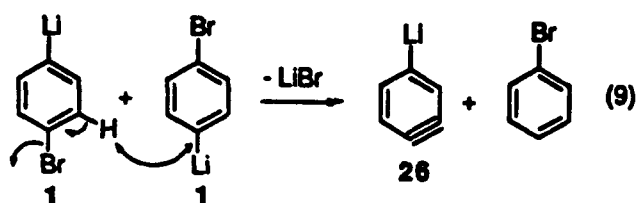


butylbenzene (0.41 mmol) and 1-bromo-4-*tert*-butylbenzene (0.16 mmol). The presence of 3,4'-bis(*tert*-butyl)biphenyl suggests that an *ortho*-benzyne intermediate was being generated. Again, no silylated material was observed in the GC thermograms. However, if bromobenzene (2 mmol) or 1-bromo-4-*tert*-butylbenzene (2 mmol) were added to *tert*-butyllithium (4 mmol) followed by warming and quenching with TMSCl, the predominant products observed in the GC analysis were, of course, the corresponding trimethylsilylbenzene and 1-*tert*-butyl-4-trimethylsilylbenzene, respectively. Since no silylated material was obtained in eqs 7 and 8, it implies that the aryllithium species, upon warming, will rapidly deprotonate the existing arylbromide to form an orthobenzyne species which is immediately trapped by a second aryllithium.

When we quenched the standard polymerizations (eq 3) with water, we noticed the rapid evolution of a gas. The gas was shown to be H<sub>2</sub> by mass spectrometric analysis. When we quenched the polymerization with D<sub>2</sub>O, DH and H<sub>2</sub> were detected. No D<sub>2</sub> was observed, thus no Li(0) forms during the polymerization. Surprisingly,

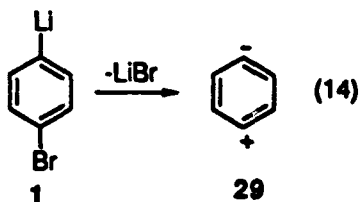
however, on quenching with D<sub>2</sub>O, the amount of DH to H<sub>2</sub> formed was 1:1.4. This was checked several times with different sources of D<sub>2</sub>O (deuterium content >99%). A large isotope effect appears to be the cause. The H<sub>2</sub> evolution on H<sub>2</sub>O quenching is probably caused by the reaction of water with LiH. Therefore, another route to *ortho*-benzynes could involve the elimination of LiH from an aryllithium species. LiH eliminations are known to occur with heterocyclic aromatics.<sup>24</sup>

Scheme V



Our results suggest that *ortho*-benzyne intermediates are involved in the polymerization and there are several possible pathways by which they may be

generated (Scheme V). One route is deprotonation of 1-bromo-4-lithiobenzene (1) resulting in the elimination of LiBr to give bromobenzene and a lithiated *ortho*-benzyne species 26 (eq 9). Presumably, bromobenzene could then undergo deprotonation by a variety of aryllithiums to give *ortho*-benzyne 27 (eq 10). Deprotonation of unreacted 1,4-dibromobenzene could also occur to give a brominated *ortho*-benzyne species 28 (eq 11). An additional route, elimination of LiH from phenyllithium or 1-bromo-4-lithiobenzene (1) may occur as well to give *ortho*-benzyne intermediates 27 and 28, respectively (eqs 12 and 13). The formation of LiH and the trapping of the *ortho*-benzyne intermediates 26, 27, and 28 suggest that all of the routes shown in eqs 9-13 are possible. At this point, however, we can not rule out the participation of an S<sub>RN</sub>1 mechanism.<sup>25</sup> Additionally, the *para*-benzyne intermediate (29)<sup>26</sup> is known and it may be forming by the loss of LiBr from 1-bromo-4-lithiobenzene (1) (eq 14). However, at this point we have no direct evidence for the intermediacy of 29 in our reaction.



In conclusion, it is apparent that this aryl-aryl coupling reaction is well-suited for the rapid preparation of a variety of halogenated polyphenylenes. The mechanism for the polymerization appears to proceed via benzyne intermediates. The solubility and high halogen content in these polymers should offer improvements in both the processing and functionalization of polyphenylenes which may open new avenues for the preparation of functionalized polyphenylene-based materials.<sup>27</sup>